NASA TECHNICAL TRANSLATION

NASA TT F-14,119

# APPLICATION OF LASER TECHNIQUES TO STUDIES OF SEMICONDUCTORS

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Translation of: "Zastosowanie techniki laserowej do badań półprzewodników", Postepy Fizyki, Vol. 22, No. 4, 1971, pp. 407-418.



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 FEBRUARY 1972

APPLICATION OF LASER TECHNIQUES TO STUDIES OF SEMICONDUCTORS

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ABSTRACT. The experimental results connected with the optical mixing and higher harmonics generation by free carriers in semiconductors, using a $CO_2$ laser, are presented.

The large enhancement of the nonlinear optical effects due to the resonance in strong magnetic fields is observed. The effect of inelastic scattering of the laser radiation due to the electrons in magnetic Landau levels in semiconductors is discussed.

## 1. Introduction /407*

The building in recent years of a molecular $CO_2$ laser emitting coherent and monochromatic radiation (10.5 μ and 9.6 μ) with a high power flux has made it possible to initiate a number of experimental investigations in the field of nonlinear semiconductor optics. These investigations cover the effects of third harmonic generation and optical frequency mixing resulting from nonlinear excitation of free current carriers by a strong electric field such as a beam of laser radiation carries with it, as well as the effects of reaction of laser radiation with bound electrons such as second harmonic generation or the phenomenon of multiphoton formation of electron-whole pairs. In semiconductors there are many more causes of optical nonlinearity than in dielectric materials. The basic causes are related to the free current carriers in the energy bands (electrons and wholes). Lax and coworkers [1] forecast that the effect of nonlinear excitation of free electrons in semiconductors is the result of the so-called nonparabolicity of the conduction band. This was demonstrated experimentally by Patel and others [2] and explained from the standpoint of theory by Wolff and Pearson [3]. Lax, Zawadzki and Weiler [4], and, independently by another means, Kolodziejczak [10], forecast increase in

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*Numbers in the margin indicate pagination in the foreign text.

the nonlinear effects on free carriers caused by resonance in strong magnetic fields.

Theoretical studies [3], [4] adopted as the point of departure the classical equation of electron motion under the influence of an oscillating electric field. The condition of nonparabolicity of the conduction band yielding the dependence of the effective mass on energy leads to nonlinear dependence of the electron velocity on momentum. Hence, in expansion of the velocity into a power series higher order (odd) expressions occur which are responsible for generation of the higher harmonics. /408

Whenever the impinging radiation is a superimposition of two monochromatic waves, corresponding mixed frequencies occur in addition to the harmonic frequencies.

In this reasoning no account was taken of decomposition of the electrons in the conduction band, and the relaxation time was assumed to be a constant parameter [3].

Kolodziejczak [5, 6, 7, 10] explained the phenomenon of nonlinear excitation of free carriers in general fashion, proceeding from the nonlinear Boltzmann equation and allowing for the density of the electron current in the presence of strong electric fields.

In the case of reaction of such fields with free carriers in semiconductors deviations from the linear law of Ohm may occur, producing in the current density oscillations which are multiples of the fundamental frequency. These oscillations cause generation of corresponding electromagnetic waves which are the higher harmonics of the incident wave.

It was demonstrated in [5, 6] that nonlinear deviations from Ohm's law are the result of two independent causes: dependence of the relaxation time on energy and nonparabolicity of the conduction band. The phenomenon of multiphoton formation of electron-whole pairs consisting in simultaneous transfer of energy through several photons requires a high photon density which only laser radiation can provide. Hence the effect of multiphoton absorption was not observed until lasers were invented. The plasma created by way of multiphoton absorption can be investigated through observations of recombination radiation [8].

## 2. Optical Frequency Mixing

The effect of third order frequency mixing caused by nonlinear excitation of free carriers was observed in single crystals of InAs, InSb, GaAs, and PbTe by Patel and coworkers [2]. A $CO_2$ molecular laser operating in the pulse mode [9] and yielding radiation of frequencies $\omega_1$ and $\omega_2$ corresponding to wavelengths respectively of $\lambda_1 = 10.6\ \mu$, $\lambda_2 = 9.6\ \mu$ was used in the study as the light of source. The observed frequencies resulting from optical mixing of the fundamental frequencies were $\omega_3 = 2\omega_1 - \omega_2$ ($\lambda_3 = 11.8\ \mu$) and $\omega_4 = 2\omega_2 - \omega_1$ ($\lambda_4 = 8.7\ \mu$). In addition, the harmonic frequency $3\omega_1$ ($\lambda = 3.53\ \mu$) was observed in InAs and GaAs. A diagram of the apparatus used for detection and /409 measurement of the power of the generated waves of the frequencies measured is shown in Figure 1.

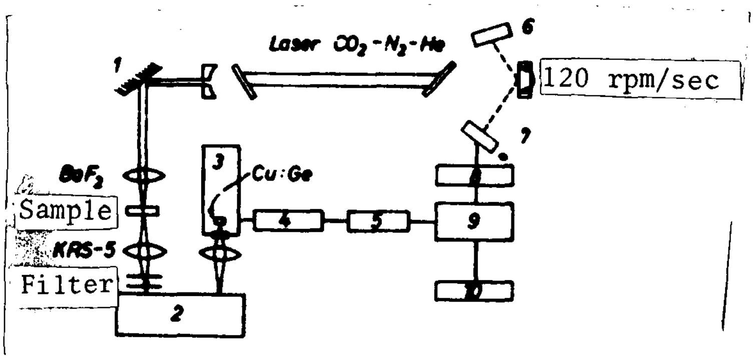


Figure 1. Diagram of Apparatus Used For Study of Effect of Optical Frequency Mixing. 1, Mirror; 2, Monochromator; 3, Helium cryostat; 4, Preamplifier; 5, Amplifier; 6, Light source; 7, Photocell; 8, Synchronizer; 9, Recorder.

Pulse operation of the $CO_2$ laser is achieved by rotation of a flat mirror at a frequency of 120 pulses/sec. Synchronization of the integrator with the laser pulse is achieved by detection of the light pulse from source 6 reflected from the rotating laser mirror. The duration of the laser pulse was around 300 nanoseconds. A germanium crystal doped with copper and operating at a temperature of 4.2°K was employed as the radiation detector. The power in the laser radiation pulse striking the sample equaled respectively $P_{\omega 1} = 1$ kW, $P_{\omega 2} = 0.1$ kW. The laser pulses are illustrated in Figures 2 c and 2 d. Figures 2 a and 2 b show radiation pulses of frequencies $\omega_3$ and $\omega_4$ generated in an InSb sample of type n ($n = 10^{17}$ $cm^{-3}$) at a temperature of 80°K. The radiation of 11.8 μ and 8.7 μ obtained had a power of 1-2 mW.

Figure 3 (curve a) shows the total intensity of the generated radiation of wavelength 11.8 μ in the type n InAs sample as a function of the electron concentration. As is to be seen, the intensity of radiation increases with increase in the concentration of free electrons. This is an argument in favor of the hypothesis that the free carriers are responsible for optical mixing effects. If the bound electrons were to cause the observed frequency mixing, the intensity of the radiation generated would then not depend on the concentration. Curve b in Figure 3 illustrates the intensity of the radiation generated at 11.8 μ as a function of the dimensions of the sample in the direction of the impinging radiation. Quadratic dependence of the power of the generated radiation on the length of the sample was observed. These measurements are in agreement with the theoretical calculations performed by Wolff and Pearson [3] for InAs of type n. These authors assumed that the free carriers are responsible for the occurrence of third order nonlinearity through increase in their effective mass in the course of acceleration by the electric field of the incident electromagnetic wave.

The equation of motion, together with the Maxwellian equations, was solved to obtain the following expression for the value of the field for frequencies $\omega_3 = 2\omega_1 - \omega_2$. /411

$$E_{\omega_3} = E_{\omega_1}^2 \cdot E_{\omega_2} \cdot \frac{3\pi N q^4}{2(m^*)^2 c \cdot n_{\omega_3}} \cdot \frac{L}{\omega_1^2 \cdot \omega_2 \cdot \varepsilon_g} \cdot \frac{1 + \frac{8\varepsilon_F}{5\varepsilon_g}}{\left(1 + \frac{4\varepsilon_F}{\varepsilon_g}\right)^{5/2}}, \qquad (1)$$

where $E_{\omega 1}$, $E_{\omega 2}$ are the electric fields for frequencies $\omega_1$, $\omega_2$; L the length of the sample; N the electron concentration; $n_{\omega 2}$ the index of refraction for frequency $\omega_3$; $\varepsilon_F$ the energy at the Fermi level; $\varepsilon_g$ the energy of the forbidden interval.

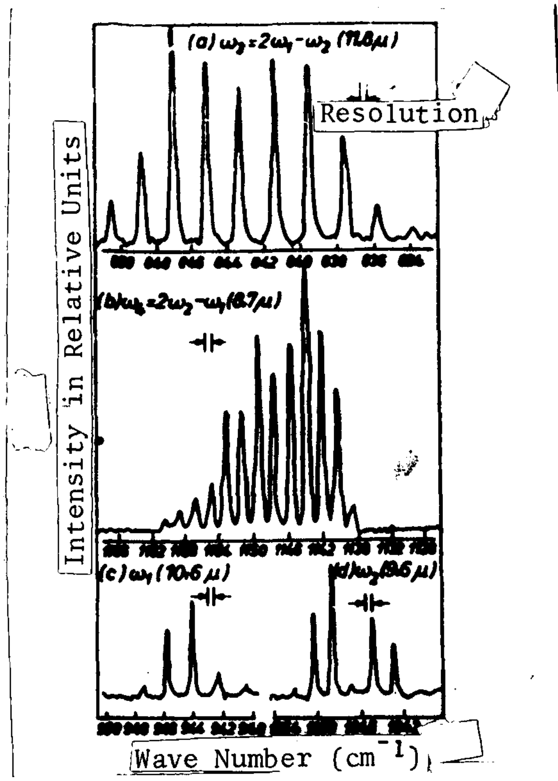


Figure 2. Radiation Pulses From Sample of InSb Type n: a) Pulses of frequency $\omega_3 = 2\omega_1-\omega_2$; b) Pulses of frequency $\omega_4 = 2\omega_2-\omega_1$; c) Pulses of $CO_2$ laser, $\omega_1$; d) Pulses of $CO_2$ laser, $\omega_2$.

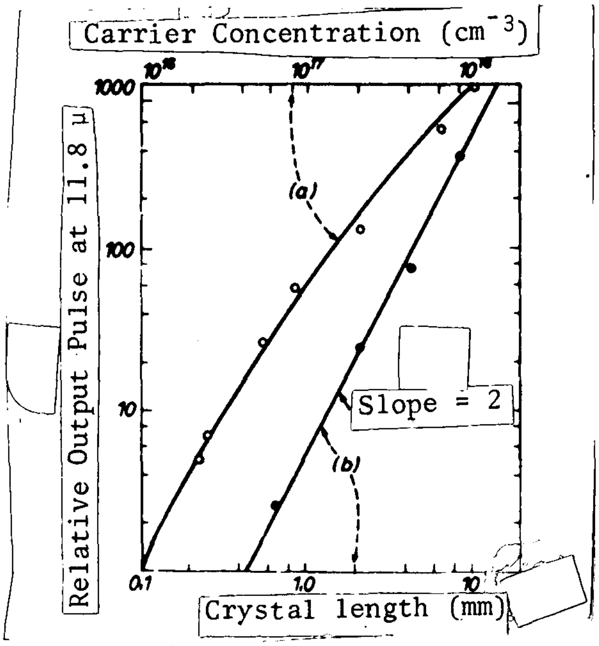


Figure 3. Pulse Versus Frequency $\omega_3 = 2\omega_1-\omega_2$ Occurring in InAs Type n from: a) Carrier concentration; b) Crystal length.

Expression (1) shows that the radiation of frequency $\omega_3$ is proportional to $L^2$. The dependence of the power on the carrier concentration is not absolutely quadratic, since for higher concentrations the effect is diminished by the second term of equation (1).

## 3. Resonance Increase of Third Harmonic and a Quantized Magnetic Field

It has been demonstrated [10], [4], that nonlinear effects may be increased in the presence of a magnetic field as a result of resonance transitions among the Landau levels. Lax, Zawadski, and Weiler [4], in considering the equation of motion for bound oscillators in a two-band nonparabolic model (assuming absence of degeneration of the valence band, a condition not fulfilled in InSb), demonstrated that increase in generation of the third harmonic occurs when

$$3\hbar\omega = [\varepsilon_g^2 + 4\varepsilon_g \hbar\omega_c(n + \tfrac{1}{2})]^{1/2}, \tag{2}$$

where $3h\omega$ is the energy of the third harmonic; $\omega_c$ is the cyclotron frequency of the electron at the bottom of the conduction band; $\varepsilon_g$ is the value of the energy interval; and n is the quantum number of the Landau level.

Figure 4 gives a schematic representation of the resonance conditions described by equation (2).

Maximum increase in third harmonic generation occurs when $3h\omega$ equals the separation energy between the Landau level in the conduction band and the Landau level in the valence band. Equation (2) applies only to a case in which Landau levels of the same quantum number n participate in the transition.

Increase in the power of the third harmonic in the presence of a magnetic field was observed by Van Trau, McFee and Patel [11]. In order to obtain radiation pulses of the fundamental frequency use was made of a $CO_2$ molecular laser yielding radiation $\lambda = 10.6\ \mu$ of a peak power of 1-5 kW (pulse time 250 nanoseconds, repetition rate 120 pulses/second). The sample investigated, having the dimensions $4 \times 4 \times 0.0015\ mm^3$, was introduced at a temperature of 15°K. The magnetic field in the range up to 54 kOe was created by a superconducting solenoid. The propagation vector of the impinging radiation and the vector of the magnetic field were directed along the smaller dimension of the sample, which had the crystallographic direction a) ⟨100⟩, b) ⟨100⟩. The carrier concentration in the sample was near $10^{14}\ cm^{-3}$. /412

Figure 5 (a, b) shows the observed increase in the relative value of the third harmonic for certain magnetic field values at which the separation energy between Landau levels equalled the quantum energy of the third harmonic. The measured values of the magnetic field (B) corresponding to the /413 extreme value of the third harmonic are given in the first column of Table 1. These values do not depend on the intensity of laser radiation.

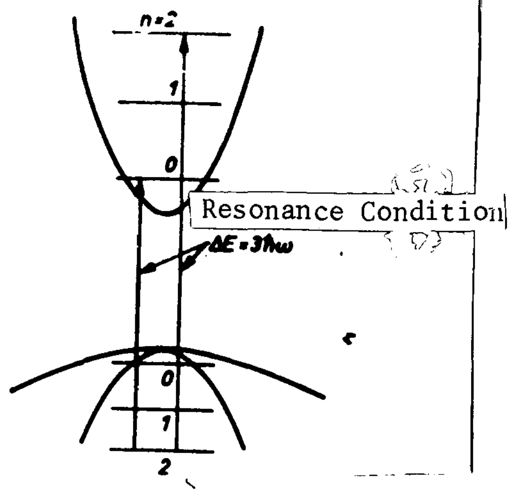


Figure 4. Diagram of Landau Levels in InSb, the Resonance Condition Being Indicated.

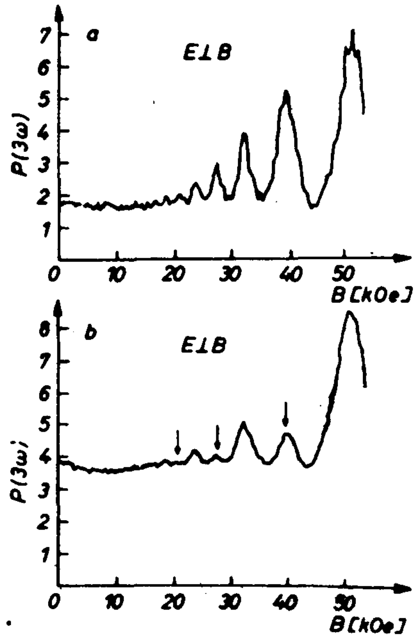


Figure 5. Power Oscillations of Third Harmonic Versus Magnetic Field.

It is interesting to compare these results with studies of magnetoabsorption between bands for InSb performed by Pidgeon and Brown [12]. For absorption between bands the radiation transmission minima occur at magnetic field values at which the energy of separation among the corresponding Landau levels equals the photon energy of the incident radiation. The magnetic field value at which occurred the transmission minima observed by Pidgeon and Brown are given in the second column of Table 1. It is to be seen that the maxima of the third harmonic occur at magnetic field values which are around 6% lower than the magnetic field values for the magnetoabsorption maxima. Such divergences were observed in investigation of the position of the maximum third harmonic values of 9.6 μ radiation.

TABLE 1.

| (1) Third Harmonic Maxima, kOe | (2) Transmission Minima for Magnetoabsorption, kOe | (3) Percentage of Divergence $\frac{(2)-(1)}{(2)} \times 100\%$ |
|---|---|---|
| 51.6 | 54.8 | 5.5 |
| 39.9 | 42.0 | 5.0 |
| 32.6 | 34.8 | 6.3 |
| 27.4 | 29.2 | 6.2 |
| 23.6 | 25.3 | 6.7 |
| 20.8 | 22.0 | 5.8 |
| 18.5 | 20.0 | 7.5 |

## 4. Multiphoton Plasma Formation and Recombination Radiation in Semiconductors

The high-intensity radiation of the $CO_2$ molecular pulse laser causes two-photon absorption, this in semiconductors with a low energy interval such as GaAs, CdA, InSb, PbTe, leading to the occurrence of electron-hole pairs, as has been demonstrated in [8].

While in GaAs, CdS, or InSb the mechanism responsible for formation of hole-electron pairs may be obscured by the possibility of generation of the second harmonic of the incident radiation and formation of electron-hole pairs by the second harmonic, experiments with PbTe provide examples of /414 existence of pure two-photon absorption (the second harmonic is virtually not generated because of the existence of an inversion center in PbTe crystals). The recombination radiation of electron-hole pairs in PbTe has been observed by use of the apparatus illustrated in Figure 6. The radiation of a $CO_2$ laser (10.6μ) of a power of around 10 kW in a pulse of a duration of 200 nanoseconds and a repetition rate of 120 pulses/second was focused on a diameter of 200 μ. The path of the recombination radiation ran through an atmosphere of nitrogen in order to eliminate absorption by water vapor. The /415 spectral decomposition of the recombination radiation obtained from PbTe of type n ($n = 10^{17}$ cm$^{-3}$) is shown in Figure 7 a.

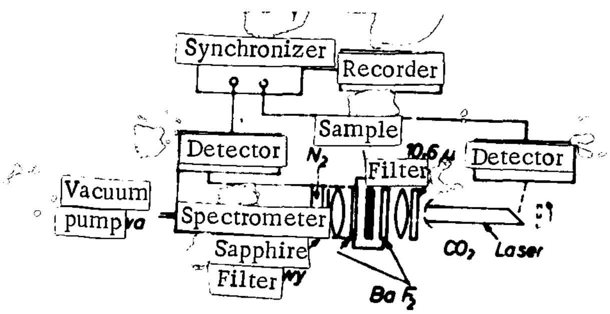


Figure 6. Diagram of Apparatus for Measurement of Recombination Radiation

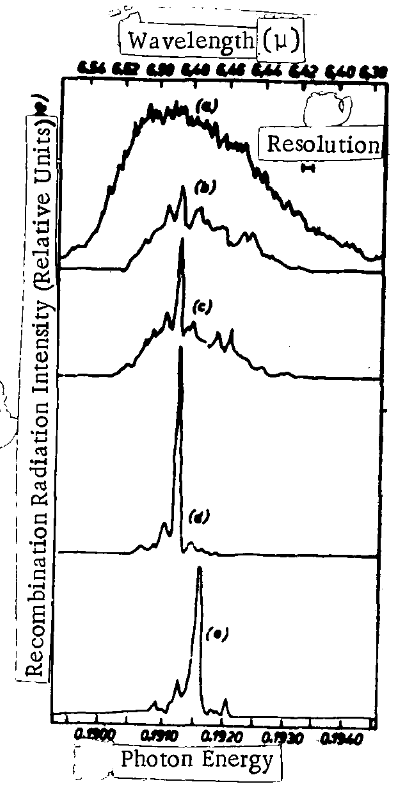


Figure 7. Spectral Decomposition of Recombination Radiation in PbTe of Type n.

The observed recombination radiation line had a power of around $3 \times 10^{-4}$ W and a spectral width of 0.002 eV. The narrow spectral width indicates that the plasma formed is of a low temperature comparable to the crystal lattice temperature. The relative intensity of the recombination radiation increased quadratically in relation to the intensity of the laser radiation, this being in agreement with the assumption of two-photon absorption. The estimated rate of formation of electron-hole pairs in the case of two-photon absorption, on the basis of calculations by Braunstein [13] for PbTe, is $W = 10^{25}\ cm^{-3}\ sec^{-1}$. Assuming that the duration of the recombination radiation $\tau_r$ is comparable to the duration of the laser pulse, and thus amounts to $10^{-8}$ sec, the density of the pairs formed as calculated from the expression:

$$N = W \cdot \tau_r \qquad (3)$$

amounts to $10^{17}\ cm^{-3}$. Laser oscillations (forced recombination radiation) were obtained in PbTe by reducing the dimensions of the focal point of the laser radiation to 50 μ.

Figure 7 b, c, d shows the spectrum of forced recombination radiation for successive 10% increases in the radiation intensity of the $CO_2$ laser. It is to be seen that at 6.486 μ the radiation carries a power substantially greater than that of recombination radiation at other wavelengths, this indicating the distance of laser oscillations. Figure 7 e shows the spectrum of recombination radiation for a higher sample temperature (120°K). The laser oscillations are displaced in the direction of the shorter waves. The coefficient of two-photon absorption for PbTe as expressed by the equation

$$\alpha\,[\mathrm{cm}^{-1}] \approx 10^{-20} \cdot E^4, \tag{4}$$

in which $E[\frac{V}{cm}]$ is the electric field of the focussed laser beam and most often equals $10^4\ \frac{V}{cm}$.

Because of the low value of a coefficient of two-photon absorption, there is only slight absorption of the impinging radiation, with the result that formation of electron-whole pairs is not restricted to the area near the surface of the semiconductor. If suitable optical pumping is employed, this can lead to laser oscillations from the entire volume of the crystals.

## 5. Inelastic Scattering of Laser Light by Electrons from Landau Levels

Study of inelastic scattering of light by electrons from Landau levels and spin sublevels can represent a source of information about the band structure of a semiconductor, by providing information on the dependence of the effective mass and spectral dispersion coefficient (g) on energy. /416
Scattering of radiation of a wavelength of 10.6 μ has been observed in InSb of type n in a magnetic field of up to 53 kOe [14]. The spectrum of the scattered radiation exhibits three clear cut lines at frequencies of $\omega_0 - \mu_B g \cdot B$, $\omega_0 - 2\omega_c$, and $\omega_0 - \omega_c$, where $\omega_0$ is the frequency of the impinging laser radiation, B the value of the magnetic field, g the effective spectroscobic dispersion coefficient of the spin sublevels, $\omega_c = \frac{eB}{m^*c}$ the cyclotron frequency, and $\mu_B$ the Bohr magneton.

Figure 8 shows typical spectral relations of light scattered in InSb of type n ($n = 5 \times 10^{16}\ cm^{-3}$) at T = 30°K for magnetic fields of (a) 26.2 kOe and (b) 36.7 kOe.

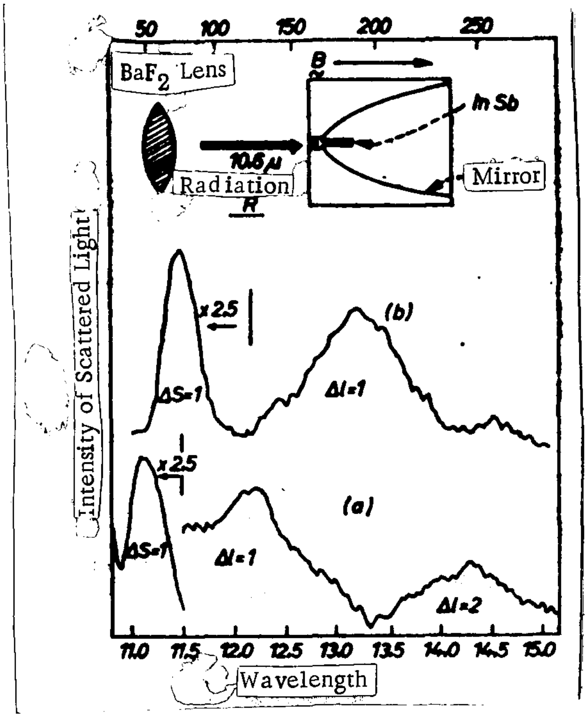


Figure 8. Spectral Decomposition of Light Scattered in InSb of Type n.

Three peaks are to be seen on curve (a), corresponding to the processes: $\Delta l = 0$, $\Delta s = 1$; $\Delta l = 1$, $\Delta s = 0$; $\Delta l = 2$, $\Delta s = 0$ ($l$ is the quantum number of the Landau level; s the quantum number of the electron spin). Curve (b) has maxima corresponding to spin transition $\Delta s = 1$ and the transition $\Delta l = 1$ displaced in the direction of the longer wavelengths because of increase in the magnetic field. The faint line at 14.5 μ was not observed in all samples; it corresponds to the transition $\Delta l = 1$, $\Delta s = 1$.

Figure 9 shows the position of the spectral lines associated with the transitions in question, as a function of the magnetic field. On the assumption of constant effective mass as a function of energy, $\Delta\nu$, understood to mean the difference between the frequency of the impinging laser radiation and the frequency of the scattered radiation, should undergo linear increase with the magnetic field. The divergence from linearity of $\Delta\nu$ plotted against the magnetic field at $\Delta l = 1$ and $\Delta l = 2$ is the degree of dependence of the effective mass on energy, the so-called degree of non-parabolicity of the conduction band. For both processes ($\Delta l = 1$ and $\Delta l = 2$) the effective mass value ranges from 0.017 m at $\Delta\nu = 160\ cm^{-1}$ to 0.02 m at $\Delta\nu = 250\ cm^{-1}$ (m is the free electron mass). For transitions associated with spin reversal ($\Delta s = 1$) divergence from the linear dependence of $\Delta\nu$ on the /417 magnetic field is the degree of dependence of the spectroscopic coefficient g on energy.

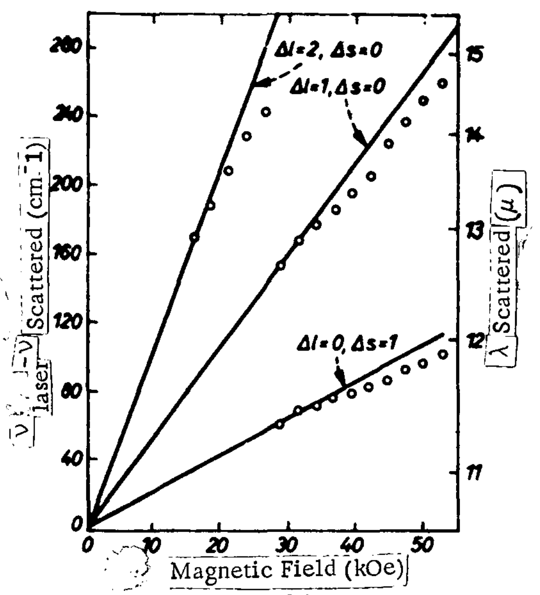


Figure 9. Wavelength of Scattered Light Versus Magnetic Field Value For InSb of Type n.

The observed values of g range from 45.8 at 26 kOe to 41.9 at kOe. They are comparable to the corresponding values obtained by Bemski [15] for a weaker magnetic field and lower concentration. Use of Zawadzki's expression [16], which relates the value of coefficient g to the effective mass value, gives m* = 0.0165 m at 26 kOe and m* = 0.018 m at 52 kOe. This change in effective mass is still in close agreement with earlier measurements [12].

The observed dependence of intensity of scattered radiation on the magnetic field is not in agreement with theoretical forecasts. The scattering for transitions associated with spin reversal ($\Delta s$ = 1) increases with the magnetic field, while Yafet [17] /418 argued that the effective cross-section for scattering of this type is virtually indpendent of the field. The quadratic dependence of the effective cross-section on the magnetic field for the process $\Delta l$ = 2, forecast by Wolff [18] has not been observed. It has been established, on the contrary, a nearly threefold decrease in the intensity of scattered radiation on change in the field from a value of 15 kOe to 26 kOe. This behavior cannot be caused exclusively by increase in absorption by free carriers for longer wavelengths. In interpretation of the foregoing results account should be taken of the change in the position of the Landau levels on increase in the magnetic field in relation to the Fermi level. Several pairs of Landau levels participate in the scattering processes, and their relative filling varies with variation in the magnetic field.

The observed effect of scattering of laser light by free electrons from Landau levels represents a convenient method of investigating such semiconductor parameters as effective mass or spectroscopic coefficient g. In contrast to resonance or absorption experiments from which such information may be obtained, in this case there is no requirement for selection of the frequency of the impinging radiation for the transition concerned, and for this reason investigation of transitions of widely varying frequencies is possible.

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Translated for the National Aeronautics and Space Administration under contract No. NASw-2031 by Techtran Corporation, P. O. Box 729, Glen Burnie, Maryland 21061, translator: H. B. Wells, Foreign Service Officer, retired.